

Conductivity of a suspension of nanowires in a weakly conducting medium

Tao Hu, A. Yu. Grosberg, B. I. Shklovskii

Department of Physics, University of Minnesota

116 Church Street SE, Minneapolis, MN 55455

(Dated: February 6, 2008)

We study macroscopic electrical conductivity of a composite made of straight or coiled nanowires suspended in poorly conducting medium. We assume that volume fraction of the wires is so large that spaces occupied by them overlap, but there is still enough room to distribute wires isotropically. We found a wealth of scaling regimes at different ratios of conductivities of the wire, σ_1 and of the medium, σ_2 , length of wires, their persistent length and volume fraction. There are large ranges of parameters where macroscopic conductivity is proportional to $(\sigma_1\sigma_2)^{1/2}$. These results are directly applicable to the calculation of the macroscopic diffusion constant of the nonspecific DNA-binding proteins in semi-dilute DNA solution.

I. INTRODUCTION

Equilibrium and transport properties of composites are of great interest because of their importance both in nature and technology. One usually wants to characterize the composite macroscopically, determining its effective properties such as conductivity, dielectric constant, magnetic permeability etc., in terms of properties of the respective constituents. Most of the theoretical literature on this subject dealt with spherical (or single scale) inclusions^{1,2,3,4,5,6,7}. At the same time, Monte-Carlo simulations and experiments reveal^{8,9,10,11,12,13,14} that elongated, needle or stick like inclusions, can be very effective in modifying the properties of materials even at small volume fractions. For example, composites made of metallic wires with aspect ratio $a/l \ll 1$ (a is the radius of the wire and l is its length) immersed in a good insulator exhibit record values of the dielectric constant¹⁵. The transport properties of such composites were studied in many works^{8,11,12,13}. A comprehensive review of these works and a thorough study of the dielectric response of conducting stick composites can be found in Ref.¹⁵, but only in the asymptotic regime of very large conductivity of wires.

Recently, another system attracted a lot of attention. It consists of carbon nanotubes dispersed in ceramic or plastic material. It was shown that nanotubes can greatly enhance the electrical and thermal conductivities of the material^{11,16,17,18,19,20}.

In this paper we present scaling theory of the macroscopic conductivity σ of the suspension of well conducting wires with conductivity σ_1 in poorly conducting medium with a finite conductivity $\sigma_2 \ll \sigma_1$. The wires can be rigid sticks or flexible and coiled like conducting polymers. We imagine that they are dispersed, randomly oriented and frozen in the medium.

On the first glance, the problem of macroscopic conductivity of the composite seems to belong to the realm of percolation⁶. Indeed, this would be true for the conducting wires in perfectly insulating medium, $\sigma_2 = 0$, where macroscopic conductivity could only be realized through the direct contacts between wires. In this article, we are interested in a different problem - we assume that the

medium does conduct, $\sigma_2 \neq 0$, albeit poorly ($\sigma_2 \ll \sigma_1$). In this case, although overall macroscopic current is carried mostly along the wires, it is still able to switch from wire to wire through the medium, depending on the random disordered configuration of the wires. Accordingly, we mostly consider volume fraction of wires ϕ to be not only small $\phi \ll 1$, but actually smaller than the corresponding percolation threshold $\phi \sim a/l$, such that the direct contacts between wires are rare and completely negligible. We show later how our results properly cross over to that of percolation at larger ϕ .

For very dilute system of wires, when the distance between wires is much larger than the length of the wire, the effective conductivity σ is trivially close to the conductivity of the medium σ_2 . We therefore mostly deal with larger concentrations with $\phi > a^2/l^2$ where the spheres containing each wire strongly overlap (see Fig. 1). In the parlance of polymer science, we study the *semidilute* system²¹ of wires. In terms of increasing concentration, our theory continues as long as there remains enough room to distribute wires isotropically. We show that although ϕ is small in semi-dilute system of wires, macroscopic conductivity σ is dramatically enhanced when compared to σ_2 .

The useful image to think about is a single typical current line in the system. It follows inside one wire for a long distance and then bridges to a neighboring wire over a more-or-less narrow gap in the medium, and then continues again in the wire for a long distance. We denote λ the length scale of one continuous stretch of current line in one wire, it can be called *correlation* length. This is the key concept of the paper. With the increase of wire conductivity σ_1 , the correlation length λ increases, and so does macroscopic conductivity σ , until λ gets as large as the wire length l , then macroscopic conductivity σ saturates at values independent on σ_1 . Remarkably, for flexible wires there are wide scaling regimes, where $\sigma \propto (\sigma_1\sigma_2)^{1/2}$. Such dependence is known for a narrow vicinity of percolation threshold in two dimensional isotropic mixtures^{1,2} but, to the best of our knowledge, has never been claimed for a broad range of parameters.

Our theory of effective conductivity of composites can be easily applied to a completely different problem, for

which the meaning of the correlation length λ is particularly obvious. Namely, we speak of diffusion of proteins through the semi-dilute system of dsDNA molecules. Many proteins have positively charged domains on their surfaces, which provide for nonspecific attraction to the negatively charged surface of the double helical DNA. Such proteins stick to DNA and diffuse along DNA for some time, then get desorbed and wander in 3D, then get adsorbed for another tour of 1D diffusion, and so on. These phenomena are believed to be behind the ability of proteins to locate their specific functional targets on DNA faster than simple 3D diffusion^{22,23,24,25}. As regards macroscopic diffusion of proteins through semidilute DNA solution, we show later in this article that this problem can be easily reduced to that of conductivity in the composite with nanowires. As a result, Fig. 2, part of Figs. 3 and 4 (which is redrawn in the Fig. 5) can all be understood in terms of macroscopic diffusion if one uses translation keys provided in the captions of these figures. The results are also summarized in Table I. Clearly, in the case of protein diffusion λ is the length of one tour of protein diffusion along DNA (including episodes of activated desorption if they are followed by correlated re-adsorption).

Our results are presented by the “phase diagrams” in the log-log plane of parameters ϕ vs. $s = \sigma_1/\sigma_2$ shown in Figs. 2, 3 and 4. They specify scaling regimes of different power laws formulae for σ listed in the Table I. Relatively simple phase diagram of Fig. 2 presents results for straight wires, while more complicated phase diagrams of Figs. 3 and 4 are constructed for semi-flexible wires characterized by a large persistence length p , such that $a \ll p \ll l$.

The plan of this article is as follows. In section II we first consider the relatively simple case when each wire is straight. In this situation we explain the main idea of our theory and identify several scaling regimes. We then consider a more complicated case when wires are flexible and coiled (section III). We continue in section IV by using these results for the macroscopic diffusion constant of proteins in semidilute DNA system. Finally, we conclude with the discussion of other possible applications of our work (section V).

In this article restrict ourselves to scaling approximation for the conductivity and to delineating the corresponding scaling regimes. In our scaling theory, we drop away both all numerical factors and, moreover, also all logarithmic factors, which do exist in the problem, because it deals with strongly elongated cylinders.

II. STRAIGHT WIRES

In this section, we concentrate on the system of straight well conducting sticks, such as, e.g., carbon nanotubes, suspended in the medium of lower conductivity - see Figure 1a. First of all let us note that percolation through the wires and the direct contacts where wires

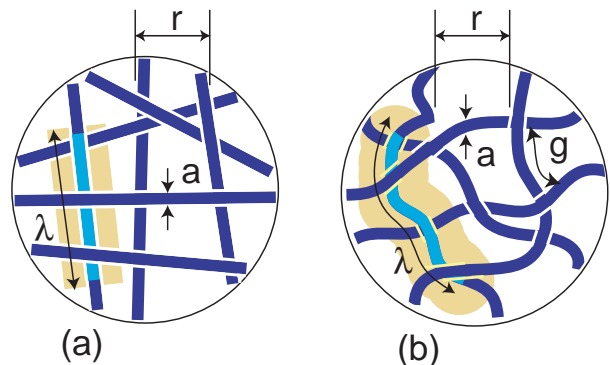


FIG. 1: Local view of the semidilute solutions of wires. The correlation length along the wire is shown in lighter color than the rest of the network. The conducting channel is shadowed. In a), wires are straight sticks. In b), wires are flexible Gaussian coils. If the mesh size is not longer than persistence length, so the wire within each mesh is essentially straight. At lesser density, the mesh size is longer than the persistence length, and then the wire in the mesh would be wiggly.

touch each other starts in such system when volume fraction of wires exceeds a critical value which is of the order of $\phi \sim a/l$ (see Ref.^{11,13}). It is not a coincidence that at about the same concentration it becomes impossible to place wires randomly and isotropically²⁶ - both percolation and nematic ordering occur at the concentration at which there are on average about two contacts per each stick.

As stated in the introduction, we consider the range of concentrations $a^2/l^2 < \phi < a/l$. Only in the very end we comment on the role of percolation in our system. As long as $\phi \ll a/l$ wires are still oriented isotropically and the contacts of wires can still be neglected, i.e., we are below percolation threshold; the latter means that overall macroscopic conductivity is entirely due to the fact that the medium does conduct, $\sigma_2 \neq 0$, albeit maybe not too well. On the other hand, the spheres containing wires already overlap strongly ($\phi > a^2/l^2$). The latter condition means that we deal with semidilute solution of sticks - the system that locally looks like a network with certain mesh size r (see Figure 1a). In the scaling sense, r is the same as the characteristic radius of density-density correlation function, and can be estimated by noticing that one stick within one mesh makes density about $\sim ra^2/r^3 \sim \phi$, therefore $r \sim a\phi^{-1/2}$.

Let us start with the simplest case when σ_1 is not significantly larger than σ_2 . Then current basically has no incentive to concentrate into the wires, instead it flows all over the place, and effective conductivity is simply that of the medium:

$$\sigma \simeq \sigma_2. \quad (\text{regime A}) \quad (1)$$

In the diagram Figure 2, this regime is denoted as A.

It is also quite easy to find perturbative corrections to the result Eq. (1) assuming small “conductivity contrast”

$(\sigma_1/\sigma_2) - 1 \ll 1$. In this case $\sigma \simeq \sigma_2 + (\sigma_1 - \sigma_2)\phi$, which follows from the fact that to the first order in perturbation the current lines remain unaffected by the difference between σ_1 and σ_2 , they remain parallel straight lines (assuming for simplicity the simplest geometry of a uniform current field), and each of them runs through σ_1 material instead of σ_2 over the fraction ϕ of its length. This perturbative result suggests that regime A continues as long as $\sigma_1\phi \ll \sigma_2$.

Let us now switch to the more challenging case, when σ_1 is so much larger than σ_2 that the current is mostly carried by the wires. To imagine the flow of current through the composite material in this case, it is useful to think of a single current line. As stated in the introduction, such line typically consists of long stretches along one wire followed by relatively short switches from wire to wire, and the important parameter is the typical length over which current line follows inside one wire, we denote it as λ .

Our plan is to consider λ as a variational parameter. That means, we first imagine the current distribution at some given value of λ , determine the resistance (or conductance) of the macroscopic sample as a function of λ , and then try to optimize λ accordingly. The justification of this procedure comes from the fact that all parts of our material obey linear Ohm's law (linear response theory), so that the requirement of minimal dissipation, or maximal overall conductance, is mathematically exactly equivalent to the Kirchhoff's laws determining distribution of currents in the network of resistors²⁷.

To begin with, let us consider the most interesting case when λ is much shorter than total length of one wire, but still larger than the mesh size r : $r \ll \lambda \ll l$. Consider then a cube of the size about λ inside our macroscopic sample. On the one hand, overall conductivity on the scale of this cube is already about the same as that of a macroscopic body, we denote it σ ; the resistance of one λ -size cube is, in other words, about $1/\lambda\sigma$. On the other hand, we can estimate this resistance considering wires inside the cube. There are about $\lambda^3/\lambda r^2$ of the wires crossing the cube, because the distance between wires is about r and, therefore, each wire can be thought of as dressed in a sleeve of the thickness about r and volume about λr^2 (see Fig. 1a). The sleeve can be thought of as a weakly leaking insulation for the wire. Each piece of the sleeve of the length about r bridges given wire to another one through the resistance about $r/\sigma_2 r^2$, and about λ/r such bridges are connected in parallel, yielding overall resistance connecting the given wire as $(1/\sigma_2 r)(r/\lambda) = 1/\sigma_2 \lambda$. This is connected in series with the wire itself, producing a conducting channel with resistance $\lambda/a^2 \sigma_1 + 1/\sigma_2 \lambda$. Since all (or sizeable fraction of all) λ^2/r^2 conducting channels in the cube are in parallel, we finally arrive at the cube resistance as $(r^2/\lambda^2)(\lambda/a^2 \sigma_1 + 1/\sigma_2 \lambda)$. Equating this to $1/\lambda\sigma$, we arrive at the following estimate of effective macroscopic

conductivity

$$\sigma \sim \frac{a^2/r^2}{1/\sigma_1 + a^2/\sigma_2 \lambda^2}. \quad (2)$$

Let us now analyze this result. As a function of λ , macroscopic conductivity does not appear to have maximum at any finite λ . This does not necessarily mean that λ is going to increase *ad infinitum*; rather, it suggests that more accurate calculation is required to determine λ . Luckily, such more accurate calculation is not necessary to determine the quantity of our interest - macroscopic conductivity σ . Indeed, as soon as λ exceeds certain threshold, namely

$$\lambda > a\sqrt{\sigma_1/\sigma_2}, \quad (3)$$

the second term in denominator of formula (2), which describes resistance of wire-to-wire bridges, becomes subdominant, and must be neglected within the accuracy of our scaling estimates. This yields

$$\sigma \simeq \sigma_1 \phi. \quad (\text{regime B}) \quad (4)$$

As expected, regimes A and B cross over smoothly on the line $\sigma_1/\sigma_2 \sim \phi$.

In the regime B, macroscopic conductivity does not depend on σ_2 , conductivity of the medium. This happens because σ_1/σ_2 is so large that current mostly flows through the wires, but at the same time σ_1 is not large enough to make resistance of wires insignificant and thus unmask the resistances of narrow gaps between wires. This is also why the resulting macroscopic conductivity is in this regime insensitive to the exact value of λ : overall distance travelled by any particular line of current through the wires scales simply as the sample size and, to the scaling accuracy, does not depend on how frequently current switches from wire to wire - precisely because wires are straight.

To complete our analysis of the regime B, let us note that the quantity $a\sqrt{\sigma_1/\sigma_2}$ which appears in the formula (3) can be understood in the following way. Imagine one straight wire in an infinite medium, and suppose we somehow feed current into a certain point 0 of this wire. Current will flow away from 0, mostly along the wire, but also slightly leaking into the environment. Due to this leaking the current remaining in the wire will decay exponentially as we move away from 0, with the decay length equal to $a\sqrt{\sigma_1/\sigma_2}$. Indeed, the length of current decay for a single wire is estimated by the condition that the resistance of wire over the length λ , which is about $\lambda/\sigma_1 a^2$, should be about the same as the resistance of the medium "in perpendicular direction", which is about $1/\sigma_2 \lambda$; equating these two returns the result (3).

Let us now switch to the next regime H, which arises because of the finite length of sticks. Indeed, the length λ , over which current flows in one wire, cannot exceed the wire length l . According to formula (3), this crossover happens along the border $s = l^2/a^2$. Indeed, starting

from this s , we get even $a\sqrt{\sigma_1/\sigma_2} > l$, and so λ cannot satisfy Eq. (3). To find conductivity in the regime H, we should replace λ by l in Eq. (2). Since the second term in the denominator dominates, we arrive at

$$\sigma \sim \phi(l/a)^2 \sigma_2. \quad (\text{regime H}) \quad (5)$$

We get the same l^2 dependence as predicted in reference¹⁵. This effective conductivity has no dependence on σ_1 because σ_1 is so high that overall resistance is entirely concentrated in the narrow gaps where current should switch from wire to wire. As a result, σ_1 does not enter the formula.

If we decrease ϕ and look at the dilute regime $\phi < a^2/l^2$, our scaling theory suggests that $\sigma \simeq \sigma_2$. More accurate analysis of this regime was performed in the work²⁸ using first order perturbation theory in powers of ϕ , which is applicable in the dilute regime, as long as current field around one wire does not affect the neighboring wires. The achievement of that work is that the authors were able to take into account, to the first order in their perturbation theory, both numerical coefficients and logarithmic factors proportional to $\ln(l/a)$ (in our notations). Up to these factors, which we systematically neglect, all our scaling results cross-over smoothly with the results of the work²⁸. Moreover, the simplified expressions of perturbation results are given in the work²⁸ in the form of three formulae, describing the dilute solution in the ranges (in our notations) $l \gg a\sqrt{\sigma_1/\sigma_2}$, $l \approx a\sqrt{\sigma_1/\sigma_2}$, and $l \ll a\sqrt{\sigma_1/\sigma_2}$; this sheds an additional light on the importance of the lengths scale $a\sqrt{\sigma_1/\sigma_2}$ introduced by us here in the present work.

Thus, we have completed our consideration of the phase diagram up to the concentration about $\phi = a/l$. It would be frustrating to stop at this point, because, for example, the experiments with suspensions of carbon nanotubes often use loadings with $\phi > a/l$ to achieve larger electrical and thermal conductivities. Let us therefore discuss what happens to conductivity if one can manage to create isotropic suspension with $\phi > a/l$. Suppose the length of wire between direct contacts, or the mesh size of the percolating network, is ζ . Then, the number of electrically parallel wires within a cube of size ζ is of the order of $\zeta^3 \phi / (\zeta a^2)$, each with the resistance about $\zeta / (\sigma_1 a^2)$. Therefore the total resistance of the cube scales as $1/(\sigma_1 \zeta \phi)$, yielding the effective conductivity about $\sigma_1 \phi$. In the scaling sense, this is the same σ as that in Regime B. Thus, regime B continues to higher concentrations $\phi > a/l$. Trivially, the lower bound of this continued regime B remains to be the condition $s > 1/\phi$, since at lower s current does not concentrate in wires, percolation gives no help. More interestingly, percolation produces no effect on conductivity σ as long as $s < (l/a)^2$ because the percolating network gives no advantage over the conducting channels made of combination of wires and surrounding medium. Percolation does have effect when $s > (l/a)^2$, where conductivity as a function of concentration ϕ changes rapidly from $\sigma \sim \phi(l^2/a^2)\sigma_2$ below percolation to $\sigma \sim \phi\sigma_1$ above. This change occurs

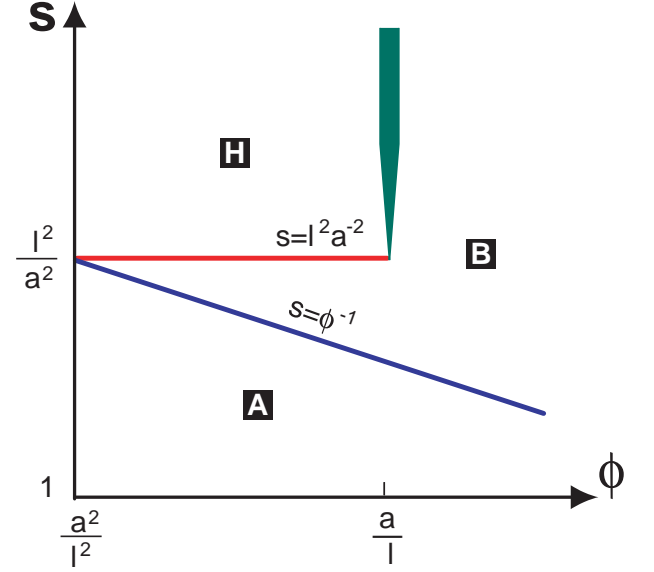


FIG. 2: Diagram of scaling regimes for the case of straight wires (e.g. carbon nanotubes). Both volume fraction of the wires ϕ and $s = \sigma_1/\sigma_2$ axes are in the logarithmic scale. Each line on this plane marks a cross-over between scaling regimes. The widened line at $\phi = a/l$ shows the location of conductivity jump around the percolation threshold. Summary of the conductivities is provided in Table I. If s is replaced by yd , the diagram represents macroscopic diffusion constant of protein discussed in section IV.

around the threshold $\phi = \phi_c \simeq a/l$, over the interval of width of order ϕ_c , which is schematically plotted as the shaded cone in the diagram Fig. 2. In this range, the conductivity has critical behavior similar to that discussed in Ref.². The detailed structure of this range is beyond the scope of this paper.

We should emphasize that in all our considerations we completely disregard the resistivity of the contacts, either between a wire and surrounding medium, or between two wires in contact. In particular, everything we said about percolation assumes that whenever there is a touch between two wires, it presents an electrical contact of vanishing resistance. In fact, this assumption is model sensitive and it is not necessarily good in practical cases. For instance, our theory predicts that above percolation threshold, when $\phi > a/l$, effective electric conductivity σ grows linearly with ϕ , independently of s being larger or smaller than $(l/a)^2$. Similar prediction holds also for thermal conductivity. However it is not compatible with the apparently super-linear growth of effective electrical or thermal conductivity observed in experiments^{17,18,19,20}. It is not clear whether interfacial resistance can help to explain these experimental data.

TABLE I: The summary of macroscopic conductivities and diffusion constants in various regimes.

Regime	σ	D
A	σ_2	D_3
B	$\sigma_1 \phi$	$D_1 y \phi$
C	$(p/a) \phi (\sigma_1 \sigma_2)^{1/2}$	$(p/a) y^{1/2} \phi (D_1 D_3)^{1/2}$
D	$(p/a)^2 \phi^{3/2} (\sigma_1 \sigma_2)^{1/2}$	$(p/a)^2 y^{1/2} \phi^{3/2} (D_1 D_3)^{1/2}$
E	$(lp/a^2) \phi \sigma_2$	$(lp/a^2) \phi D_3$
F	$(lp^3/a^4) \phi^2 \sigma_2$	$(lp^3/a^4) \phi^2 D_3$
G	$(p/a) \phi^2 \sigma_1$	no correspondence
H	$(l^2/a^2) \phi \sigma_2$	$(l^2/a^2) \phi D_3$

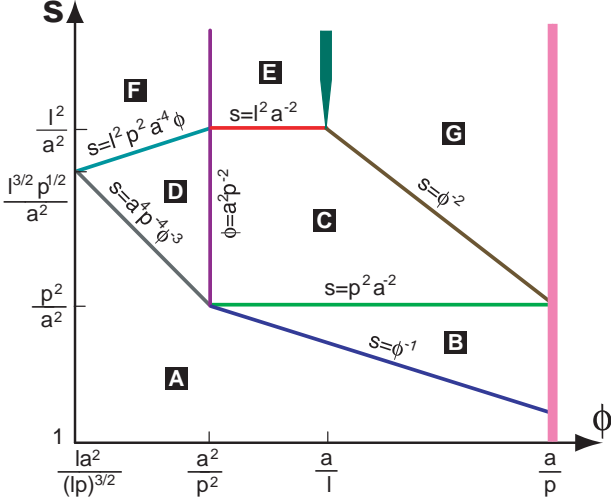


FIG. 3: Diagram of scaling regimes for the case of flexible Gaussian coiled wires (e.g. conducting polymers) with length $p < l < p^2/a$. Summary of the conductivities is provided in Table I.

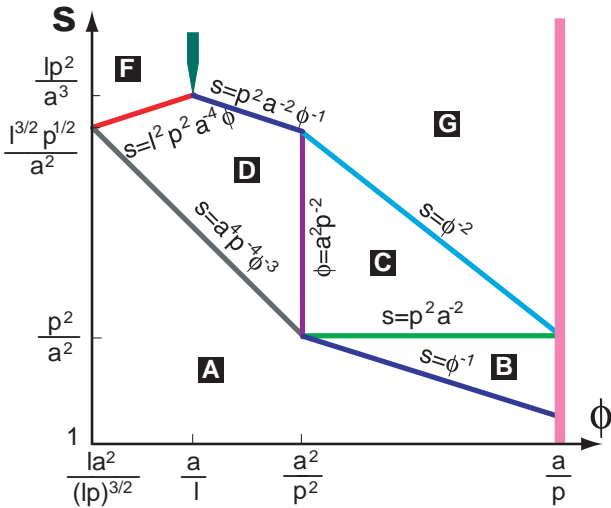


FIG. 4: Diagram of scaling regimes for the case of flexible Gaussian coiled wires with length $p^2/a < l < p^3/a^2$.

III. GAUSSIAN COILED WIRES

When wires are flexible (e.g. conducting polymer), our theory developed in section II needs modifications to account for different fractal properties of the wires. We consider the system of semi-flexible conducting polymers as an example (see Fig. 1b). We assume that each polymer has contour length l , relatively large persistence length p and the radius (thickness) a . We assume $l \gg p \gg a$. Throughout this work we require $l < p^3/a^2$ and this lets us disregard the effect of excluded volume on the polymer statistics, considering polymer coil as Gaussian. Therefore, if we take a piece of polymer of the contour length λ , then its size in space scales as

$$\xi \sim \begin{cases} \lambda & \text{when } \lambda < p \\ \sqrt{\lambda p} & \text{when } \lambda > p \end{cases} \quad (6)$$

The overlap of coils starts when the volume fraction of polymers exceeds volume fraction of the chain inside one coil: $\phi \sim la^2/(lp)^{3/2} = a^2/(l^{1/2}p^{3/2})$. The nematic ordering of wires starts at a larger volume fraction $\phi \sim a/p$. The percolation threshold can be estimated from following argument. Percolation happens when each wire has roughly two direct contacts with other wires. Following Ref.²¹, the number n of contacts per wire is of the order of

$$n \sim \phi l/a \quad (7)$$

(each piece of the polymer of the length a has probability ϕ to be in touch). Requiring that n is of the order of 1, we obtain the percolation threshold $\phi_c \sim a/l$. Percolation starts earlier than the nematic ordering and ϕ_c , because percolation requires a couple of contacts per wire, while nematic ordering requires a contact per a smaller length of a statistical segment ($\sim p$). Therefore, ϕ_c divides into two parts the range of concentrations when the system is semi-dilute but isotropic $a^2/(l^{1/2}p^{3/2}) < \phi < a/p$: $a^2/(l^{1/2}p^{3/2}) < \phi < \phi_c$ where we neglect the effect of direct contacts; and $\phi_c < \phi < a/p$ where the effect of the percolating wires must be included in our theory.

Let us start with determining the mesh size r ²¹. Suppose that the polymer within each mesh has a contour length g . It makes a density about $\sim ga^2/r^3$ which must be about the overall average density ϕ . Thus, $ga^2/r^3 \sim \phi$. Second relation between g and r depends on whether mesh size is bigger or smaller than persistence length p :

$$r \sim \begin{cases} g & \text{if } g < p \\ \sqrt{gp} & \text{if } g > p \end{cases} \quad (8)$$

Accordingly, one obtains

$$\begin{aligned} g &\sim a\sqrt{\frac{1}{\phi}}, \quad r \sim a\sqrt{\frac{1}{\phi}} & \text{if } \frac{a}{p} > \phi > \frac{a^2}{p^2} \\ g &\sim \frac{a^4}{\phi^2 p^3}, \quad r \sim \frac{a^2}{\phi p} & \text{if } \frac{la^2}{(lp)^{3/2}} < \phi < \frac{a^2}{p^2} \end{aligned} \quad (9)$$

The upper line corresponds to such a dense network that every mesh is shorter than persistence length and polymer is essentially straight within each mesh (see Fig. 1b). The lower line describes much less concentrated network, in which every mesh is represented by a little Gaussian coil. Depending on the relation between l and p , percolation can start before or after $\phi \sim a^2/p^2$. Our results for these two cases are summarized in Figs. 3, 4 and in the Table I.

When the correlation length $\lambda < p$, the polymer within correlation length is straight. So we can directly apply what we got for the straight wire case and obtain regimes A and B.

For other regimes with $\lambda > p$, the derivation has to be performed from the beginning. So, we consider a typical cube inside the composite with size ξ such that every polymer enclosed in this cube has contour length of the order of correlation length λ . There are about $\frac{\xi^3}{r^3(\lambda/g)}$ electrically parallel conducting channels in this cube (because λ/g is the number of meshes visited by one wire, and r^3 is the volume of each such mesh). Each channel consists of the wire itself, with resistance $\lambda/(\sigma_1 a^2)$, and the wire is connected in series with the group of λ/g parallel connected bridges, each of resistance $r/(\sigma_2 r^2)$. Thus, the resistance of the cube scales as

$$\frac{\lambda/(\sigma_1 a^2) + g/(\sigma_2 \lambda r)}{g \xi^3/(\lambda r^3)}, \quad (10)$$

which should be equated to $1/(\sigma \xi)$. Therefore we obtain:

$$\sigma \simeq \frac{a^2 g / r^3}{\lambda^2 / (\sigma_1 \xi^2) + g a^2 / (\sigma_2 r \xi^2)}. \quad (11)$$

Once again, if the wire remains straight over the length λ , so that $\xi \simeq \lambda$, we are back at the situation described by formula (2), and we can reproduce the corresponding result for the regime B, (4). More interestingly, we can now consider the case when $\lambda > p$ and the polymer of the length λ is the Gaussian coil: $\xi \sim \sqrt{\lambda p}$. In this case we obtain

$$\sigma \sim \frac{p a^2 g / r^3}{\lambda / \sigma_1 + a^2 g / (\sigma_2 r \lambda)}. \quad (12)$$

Now conductivity has the well defined maximum at the well defined value of λ :

$$\lambda \sim a \left(\frac{\sigma_1 g}{\sigma_2 r} \right)^{1/2}. \quad (13)$$

Not coincidentally, this result for the correlation length λ corresponds to equating two terms in the denominator of Eq. (12) - the resistance of wire with correlation length λ and the resistance of the surrounding "sleeve" of thickness r in the medium.

Plugging λ from Eq. (13) back into Eq. (12) and applying Eqs. (9), we obtain the following two scaling regimes:

Regime C, where polymer on the scale λ is Gaussian (lower line in the Eq. (6)), but the polymer within each mesh is still straight;

Regime D, where polymer is Gaussian even within each mesh (lower lines in the Eqs. (9)).

When λ reaches the entire length of the polymer l , we should replace λ by l in Eq. (12). Then the second term in the denominator dominates. Since we have two different kinds of meshes represented by formulae (9), we have two more regimes:

Regime E, where $\lambda = l$ and the polymer within each mesh is straight (upper lines in the Eq. (9));

Regime F, where $\lambda = l$, but the polymer within each mesh is Gaussian (lower lines in the Eq. (9)).

We should emphasize that regime E exists only in the case where $l < p^2/a$ (see Fig. 3). If $l > p^2/a$, percolation starts so early that the polymer within each mesh is a Gaussian coil. This case is plotted in Fig. 4.

When we increase σ_1/σ_2 , the effective conductivity grows from σ_2 (regime A) and finally saturates in regimes E and F with values having no dependence on σ_1 . As we discussed, for regime A, transport through wires is not at play while in regimes E and F, σ_1 is so large compared to σ_2 that the wires are effectively "superconducting". More interestingly, for broad ranges of ϕ and σ_1/σ_2 (regimes C and D), σ is proportional to $\sqrt{\sigma_1 \sigma_2}$. Such dependence is known for a narrow vicinity of percolation threshold in isotropic mixtures¹ but, as far as we know, it has never been noticed for a broad range of parameters. The width of the range grows as l^2 .

When the volume fraction is larger than the percolation threshold, the effect of percolating wires can not be neglected. If σ_1/σ_2 is relatively small, the transport of current is mainly realized through the conducting channel we have discussed. But when σ_1/σ_2 is large enough, percolation through the directly connected wires dominates. The crossover is determined by equating the conductivity due to the untouched wires and surrounding medium and the conductivity due to percolating wires. We have already calculated the first conductivity. The later one can be calculated by the following argument. Let us denote the length of wire between contacts by ζ . It can be estimated as $\zeta \sim l/(\phi/\phi_c) \sim a/\phi$. Because we require $\phi < a/p$, ζ is larger than the persistence length p and thus the distance it covers in space scales as $\sim (\zeta p)^{1/2}$. Within a cube with size $(\zeta p)^{1/2}$, there are $(\zeta p)^{3/2} \phi / (\zeta a^2) \sim (p/a)^{3/2} \phi^{1/2}$ electrically parallel wires. So the conductance scales as $\sigma_1 p a / \zeta$. It can be also expressed using effective conductivity, it is $\sigma (\zeta p)^{1/2}$. Comparing these two conductances, we obtain $\sigma \sim (p/a) \phi^2 \sigma_1$, which is the effective conductivity in regime G. It crosses over smoothly to the regimes E and F (E only exists for case $l < p^2$, which is represented in Fig. 3). One can also obtain the border by equating the correlation length λ to the length between direct contacts ζ . Since we assume the current can switch wires freely at the contacts, λ can not grow above ζ . On the other hand in the scaling approach we use, there is a conductivity jump around

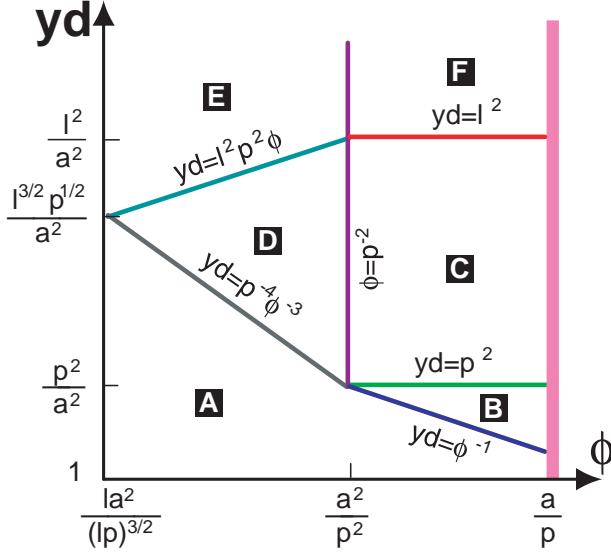


FIG. 5: Diagram of scaling regimes for the case of protein diffusion in Gaussian coiled DNA solution. Summary of the macroscopic diffusion constants is provided in Table I.

the percolation threshold $\phi_c \sim a/l$, which is plotted as the widened line in both figures. Actually the jump of conductivity is eliminated when we consider the critical behavior of conductivity at $\phi - \phi_c \ll \phi_c$ but our scaling theory is not designed to see such details.

IV. MACROSCOPIC DIFFUSION CONSTANT OF PROTEINS IN SEMIDILUTE DNA SYSTEM

The theory we have developed for the effective conductivity of composites can be used to study the macroscopic diffusion constant of the nonspecific DNA-binding proteins in semidilute DNA solutions.

For simplicity, we make the following assumptions: (i) protein can be non-specifically adsorbed on any place of DNA; (ii) non-specific adsorption energy ϵ , or the corresponding constant $y = e^{\epsilon/k_B T}$, are the same everywhere along DNA (sequence-independent); (iii) every protein molecule has just one surface patch capable to stick to the DNA, so proteins do not serve as cross-linkers for the DNA; (iv) non-specifically bound protein can diffuse along DNA with the diffusion coefficient D_1 , while protein dissolved in surrounding water diffuses in 3D with diffusion constant D_3 ; (v) while protein is diffusing, the DNA remains immobile.

To make the dictionary of translation between conductivity and diffusion languages, the easiest way is to step up the generality in writing down the expressions for current density \mathbf{j} in either conductivity or diffusion problem. In both cases, as long as we consider stationary process, current is subject to the no-divergence condition: $\text{div} \mathbf{j} = 0$. For the electric current driven by the potential

gradient, Ohm's law reads $\mathbf{j} = -\sigma(\mathbf{x})\nabla\phi$; and for the diffusion problem, current driven by the gradient of total chemical potential is described by similar Smoluchowski equation: $\mathbf{j} = -D(\mathbf{x})c(\mathbf{x})\nabla(\ln c(\mathbf{x}) - \epsilon(\mathbf{x})/k_B T)$. Here, we assume for a moment, that electrical conductivity, diffusion coefficient, protein concentration c , and binding energy ϵ or $y = e^{\epsilon/k_B T}$ have all some general dependence of space coordinates \mathbf{x} . In fact, for our case, this space dependence is very simple: within narrow regions along the wires or along DNA, we have $\sigma(\mathbf{x}) = \sigma_1$, and similarly $D(\mathbf{x}) = D_1$ and $y(\mathbf{x}) = y$ (remember that $y = e^{\epsilon/k_B T}$); for all other places \mathbf{x} we have $\sigma(\mathbf{x}) = \sigma_2$, $D(\mathbf{x}) = D_3$ and $y(\mathbf{x}) = 1$. As regards concentration, diffusion equation also implies (since chemical potential is continuous) that locally there is the equilibrium relation between the 1D concentration of non-specifically adsorbed proteins, c_1 , and concentration of proteins remaining free in the nearby solution c_3 :

$$c_1/(c_3 a^2) = y, \quad (14)$$

where a is the length scale such that c_1/a^2 is the 3D concentration of proteins within the region around DNA where proteins are adsorbed. Comparing the equations, we see that complete mapping is achieved by the substitutions $\sigma_1 \leftrightarrow D_1 c_1/a^2$, $\sigma_2 \leftrightarrow D_3 c_3$. Similarly writing the effective macroscopic equations in terms of macroscopic conductivity σ and macroscopic diffusion coefficient D , one finds $\sigma \leftrightarrow D c_3$. In terms of more convenient dimensionless quantities, and taking into account the local adsorption equilibrium (14), these rules read:

$$\frac{\sigma_1}{\sigma_2} \leftrightarrow \frac{D_1}{D_3} y, \quad \frac{\sigma}{\sigma_2} \leftrightarrow \frac{D}{D_3}. \quad (15)$$

We can, therefore, directly address macroscopic diffusion based on our results for macroscopic conductivity. Substituting Eq. (15) into our results for σ , we obtain the macroscopic diffusion constants of the proteins in the DNA solution expressed in terms of D_1 and D_3 for all the regimes except regime G, for which the applicability of percolation results to the DNA case is doubtful.³⁰

Thus, Fig. 2 can be used for the macroscopic diffusion constants for the straight DNA case if we replace σ_1/σ_2 by yD_1/D_3 . However, for the gaussian coiled DNA case, without regime G, Figs. 3 and 4 should be modified. Resulting phase diagram is shown in Fig. 5. One can easily get this figure from Fig. 3 by removing the borders the regime G makes with other regimes and extending the border line between regimes E and C to the right boundary of the phase diagram. The results for various scaling regimes are also summarized in the right most column of Table I.

Measuring macroscopic diffusion of proteins is a promising way to test our predictions. It is therefore useful to comment a little deeper on the nature of macroscopic diffusion coefficient D . The way it is defined above is adequate for a macroscopic experiment, because D establishes the proportionality between the flow of proteins

and the gradient of concentration of *dissolved* proteins. In such experiment, the presence of a large number of proteins adsorbed on DNA is not directly relevant. However, in a different experiment, for instance, in tracking the random walks of a single protein molecule, a different diffusion coefficient, \tilde{D} , will be relevant, such that $\tilde{D}c = Dc_3$, where c is total concentration of proteins, including the adsorbed ones: $c = (c_1/a^2)\phi + c_3(1 - \phi)$. Using (14), one then gets $\tilde{D} = D/(1 - \phi + y\phi)$. The difference between these two diffusion coefficients is marginal when absorption is weak ($y \ll 1$ and $\phi \ll 1$), but it becomes very much pronounced when the absorption is strong, or y is large: $\tilde{D} \simeq D/(y\phi) \ll D$. This result has simple physical meaning: every particular protein will be adsorbed most of the time, so its diffusive motion will be slow, but overall flow of proteins will not be that slow because of a large number of proteins.

Using the macroscopic diffusion constant, we can also re-derive the results of the work²⁵ concerning the rates of protein searching for specific places on globular DNA. Thus, measuring D or \tilde{D} is another way to verify the results of Ref.²⁵ in those crowded regimes.

V. CONCLUSION

In this paper we studied a plethora of different scaling regimes for conductivity of a suspension of wires in poorly conducting medium. Our results are applicable to suspensions of metallic wires in poorly conducting medium at room temperature. In this case our generic description of the system only by two macroscopic local conductivities is valid, because typically the surfaces of nanowires are so dirty that any surface barrier for electrons of the metal is sufficiently well conducting due to hopping through localized states.

We also mention carbon nanotube suspensions as a possible application of our theory. In this case one may worry about the role of the surface resistance on the nanotube-medium interface, so that our theory strictly speaking only estimates the effective conductivity from above. Including surface resistance or allowing for influence of environment on conductivity of nanotubes would require new parameters in the theory, making it much more complicated. We believe that both real and computer experiments should be first compared with the simplest and generic model presented here in this paper before one starts developing more complicated theories.

The serious advantage of our generic theory is that it can be applied in a variety of different problems beyond electric conductivity, for instance, to thermal conductivity of well thermally conducting wires in a weaker thermally conducting medium, to macroscopic dielectric constant of suspended metallic wires and to wires with large magnetic susceptibility. We also applied our theory to the calculation of the macroscopic diffusion constant of the nonspecific DNA-binding proteins in semi-dilute DNA solution.

The latter application is also promising in terms of computational tests of our theory along the lines of the recent work^{24,29}.

Acknowledgments

We are grateful to D. J. Bergman, M. Foygel, M. Fogler, V. Noireaux and A. K. Sarychev for useful discussions. The work of AG was supported in part by the MRSEC Program of the National Science Foundation under Award Number DMR-0212302. The work of AG and TH was supported in part by the grant from the US-Israel Binational Science Foundation, Award 2004251.

-
- ¹ A.M. Dykhne, Zh. Eksp. Theor. Phys. **59**, 111 (1970).
 - ² A.L. Efros and B.I. Shklovskii, Phys. Stat. Sol. B **76**, 476 (1976).
 - ³ D.J. Bergman and D. Stroud, Solid State Phys. **46**, 147 (1992).
 - ⁴ G.A. Niklasson and C.G. Granqvist, J. Appl. Phys. **55**, 3382 (1984).
 - ⁵ J.P. Clerc, G. Giraud and J. M. Luck, Adv. Phys. **39**, 191 (1990).
 - ⁶ D. Stauffer and A. Aharony, *Introduction to Percolation Theory*, 2nd ed (Taylor & Francis, London, 1992).
 - ⁷ F.G. Shin and Y.Y. Yeung, J. Mater. Sci. Lett. **7**, 1066 (1988).
 - ⁸ I. Balberg, N. Binenbaum, C. H. Anderson, Phys. Rev. Lett. **51**, 1605 (1983).
 - ⁹ I. Balberg, Phys. Rev. B **31**, 4053 (1985).
 - ¹⁰ I. Balberg, Phys. Rev. B **33**, 3618 (1986).
 - ¹¹ M. Foygel, R.D. Morris, D. Anez, S. French and V.L. Sobolev, Phys. Rev. B **71**, 104201 (2005).
 - ¹² C.A. Zuev and A.F. Sidorenko, Teor. Mat. Fiz **62**, 76 (1985); 253 (1985).
 - ¹³ A.N. Kolesnikov, A.N. Lagardov, L.N. Novogrudskiy, S.M. Matitsin, K.N. Rozanov, and A.K. Sarychev, in *Optical and Electrical Properties of Polymers*, edited by J. A. Emerson and J. M. Torkelson, MRS Symposia Proceedings No. 214 (Materials Research Society, Pittsburgh, 1991), p. 119.
 - ¹⁴ Y. Yagil, P. Gadenne, C. Julien, G. Deutscher Phys. Rev. B **46**, 2503 (1992).
 - ¹⁵ A.N. Lagarkov and A.K. Sarychev, Phys. Rev. B **53**, 6318 (1996).
 - ¹⁶ R. Andrews, D. Jacques, A. M. Rao, T. Rantell, F. Derbyshire, Y. Chen, J. Chen and R. C. Haddon, Appl. Phys. Lett. **75**, 1329 (1999).
 - ¹⁷ S. Choi, Z.G. Zhang, W. Yu, F.E. Lockwood and E.A. Grulke, Appl. Phys. Lett. **79**, 2252 (2001).
 - ¹⁸ C. Park, Z. Ounaies, K.A. Watson, R.E. Crooks, J. Smith, Jr., S.E. Lowther, J.W. Connell, E.J. Siochi, J.S. Harrison and T.L. St. Clair, Chem. Phys. Lett. **364**, 303 (2002).
 - ¹⁹ M.B. Brynning, D.E. Milkie, M.F. Islam, J.M. Kukkawa,

- A. G. Yodh, Appl. Phys. Lett. **87**, 161909 (2005).
- ²⁰ B.E. Kilbride, J.N. Coleman, J. Fraysse, P.Fournet, M.Cadek, A. Drury, S. Hutzler, S. Roth and W.J. Blau, J. Appl. Phys. **92**, 4024 (2002).
- ²¹ A.Yu. Grosberg, A. Khoklov, *Statistical Physics of Macromolecules* (AIP Press, New York, NY, 1994).
- ²² O.G. Berg, R.B. Winter and P.H. von Hippel, Biochemistry **20**, 6929 (1981).
- ²³ S.E. Halford and M.D. Szczelkun, Eur. Biophys. J. **31**, 257 (2002).
- ²⁴ K.V. Klenin, H. Merlitz, J. Langowski and C.X. Wu, Phys. Rev. Lett. **96**, 018104 (2006).
- ²⁵ Tao Hu, A. Yu. Grosberg and B. I. Shklovskii, Biophys. J. **90**, 2731 (2006).
- ²⁶ L. Onsager, Ann. N.Y. Acad. Sci. **51**, 627 (1949).
- ²⁷ I. Prigogine, *Thermodynamics of Irreversible Processes* (Interscience, New York, 1961).
- ²⁸ X. Zheng, M.G. Forest, R. Lipton, R. Zhou and Q. Wang, Adv. Funct. Mater. **15**, 627 (2005).
- ²⁹ H. Merlitz, K.V. Klenin, C.X. Wu, J. Langowski. physics/0602113.
- ³⁰ As we mentioned, even for the wires the idea of direct contact is very much model-dependent. It is even more so for the protein and DNA case, because in this case “contact between wires” should mean the possibility for the protein to switch from one DNA to the other without activation. It might be possible in some systems but impossible in others; besides, there are quite a few other effects which are beyond our theory, such as excluded volume constraints for the proteins which becomes significant when two DNA pieces are close by - protein may have difficulties diffusing along one of them, like a big truck under a low bridge on a highway. We do not consider all these questions in this paper, and only consider DNA system well below percolation threshold.